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Sorption of cd (II) ions by chitosan modified peanut shell biochar from aqueous solution

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ABSTRACT

In this paper, biochar was prepared from peanut shells, and then the pristine biochar (PBc) was modified by chitosan (CBc). The characteristics of the absorbents were investigated using infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and Brunauer, Emmett and Teller analysis (BET). The effects of the biochars dosage, pH, initial cadmium concentration, and contact time on cadmium removal were evaluated. Adsorption isotherms and kinetic models were used to explain the adsorption process. The results indicated that CBc could be used as a biosorbent for the removal of heavy metals from the aqueous solution. The adsorption data conformed best to the Langmuir isotherm. Optimum conditions for the highest removal of Cd (II) were obtained at the biochar dosage of 0.6 g/L, 30 mg/L initial concentration of Cd (II) solution, pH value of 6, and within 30 minutes. The maximum adsorption capacities of pristine and modified biochar were found to be 40 mg/g and 58.823 mg/g, respectively. The kinetic data displayed that pseudo-second-order kinetic model can well fit the process of cadmium biosorption. The coatings of biochar with chitosan can greatly improve the absorbent efficiency in the removal of heavy metals and the chitosan-modified biochar can be used as a, low-cost, effective and environmental-friendly adsorbent.

1. Introduction

Cadmium is one of the most toxic heavy metals that often enters into the aquatic environment via various sources. Such heavy metals easily accumulates in the environment and biosystems because they are mobile in soil or water, and they have a non-biodegradable nature [34]. Heavy metals threaten the health of humans and animals by way of the food chain. Since humans are nearer the top of the food chain, they are more at risk. That's why heavy metal contamination has been a serious problem [20]. Recently, different methods including precipitation [32], ion exchange [3], electrochemical techniques [5,28], membrane filtration [9], and adsorption [14,15] have been applied to remove heavy metals. Among these methods, adsorption is one of the most reputable approaches owing to its high-performance and affordability [26,36]. Iran produces peanuts at the rate of 30 thousand tons per year and increases annually. The peanut shells are thrown away or burned and causes pollution. Many researches have shown that biochar from peanut shell has great potential for heavy metals remediation from contaminated water [4,7]. Nowadays, modification of biochar with chemical reagents has been developed to further enhance the adsorption ability of biochar in the removal of heavy metals [42-43]. Chitosan is one of the most abundant natural polysaccharides in the world that is obtained by deacetylation of chitin. It is found in the exoskeletons of crustaceans and is a non-toxic, inexpensive, widely available, high binding capacity, and renewable product [19,31,35]. Chitosan, surface modification and remediation agent, has been used to modify surfaces of adsorbents because its functional groups have a strong bonding ability to various heavy metal ions [11]. Zhou, Zhou, Liu, Guo, Ren and Zhou [46] reported the modification of biochar using

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hydrogen peroxide and Fe_3O_4 nano-particles for the removal of cadmium. Xiang, Lin, Cheng, Guo, Yao, Liu, Yin and Liu [40] found that the presence of MgO nanoparticles on biochar surfaces can improve the adsorption performance of cadmium. Wongrod, Simon, van Hullebusch, Lens and Guibaud [39] report that the activation of biochar by potassium hydroxide or hydrogen peroxide enhanced the sorption ability to arsenic and chromium. Biochar produced from different feedstock has been widely researched, but the application of chitosan modified peanut shell biochar for heavy metals removal has yet to be studied. The aim of this study is the preparation of biochar from peanut shells and its modification using chitosan. The sorption ability of absorbents has been evaluated for the removal of Cd (II) ion from aqueous solution. The obtained products have been characterized by FTIR, SEM, BET, adsorption isotherms, and kinetic models.

2. Materials and methods

2.1. Preparation of biochar and modified biochar using chitosan

Peanut shells were collected from Astaneh Ashrafieh, a city in Gilan-Iran province. After washing and drying, these materials were crushed by electric mills into smaller pieces. For the preparation of the biochar, the material was first passed through a 1 mm sieve; then, slow pyrolysis is carried out at 450 °C for four hours with a heating rate of 10 °C/min and 30 min residence time in a carbonization furnace. To modify the biochar, three grams of chitosan (Sigma-Aldrich-molecular weight is 190000 Da) was dissolved in 180 ml of acetic acid (Merck, Germany), and three grams of biochar was added to it. The mixture was stirred for 30 minutes, and the homogeneous suspension was added dropwise to 900 ml sodium hydroxide (1.2% Merck, Germany) and placed for 12 hours. The modified biochar was washed with deionized water to remove the excess sodium hydroxide, and finally dried at 70 °C for 24 hours [47]. The elemental C, N, and H contents of the samples were determined via a CHN elemental analyzer (PerkinElmer series II 2400). The surface morphology of the biochar and the chitosan-modified biochar was characterized by the scanning electron microscope (FESEM-MIRA III TESCAN). Functional groups of the samples were determined by Fourier transform infrared (FTIR- Perkin Elmer). The specific surface area, pore-volume, and pore size of samples were calculated by Brunauer Emmett Teller (BET- BELSORP MINI II BEL) analysis.

2.2. Absorbent equilibrium studies

The effect of contact time on the rate of adsorption of the cadmium from water was tested. To investigate the effect of the reaction time on the adsorption of cadmium from water, 0.03 g of biochar was added to 50 ml of the solution containing 30 mg/L of cadmium. Then, the solution was placed on a shaker at a speed of 110 rpm. After five to 35 minutes, the solution was centrifuged for 20 minutes at a rate of 4000 rpm and filtered. Finally, the cadmium concentration in the solutions was read by the atomic adsorption device. The effect of the biochar dosage on the removal of cadmium (30 mg/L) from the water was investigated by contacting 50 ml of cadmium solution (30 mg/L) at room temperature for 35 min., various amounts of biochar (0.1- 1 g/L) were used. The effect of different pH values (2-8) on the removal of cadmium was studied. The pH values of solutions were adjusted by hydrochloric acid and sodium hydroxide. The sample (0.6 g/L) was added to 50 ml of cadmium solution (30 mg/L), and the concentration of cadmium present in the solution was read by atomic absorption. The removal percentage of Cd (II) was calculated according to the difference of the equilibrium (C_e) and initial concentration (C_i) of Cd (II) in solution (mg/L), per Eq. 1:

$$\%\,Removal = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

The adsorption capacities q_t (mg/g) were determined from the following, per Eq. 2:

$$q_t = \frac{(C_i - C_t)V}{W} \quad (2)$$

where C_i and C_t (mg/L) are the initial and equilibrium concentrations of Cd (II) in solution, respectively, V (L) is the volume of the Cd (II)solution, and W (g) is the mass of the adsorbent [24].

2.3. Isotherms study

The Langmuir, Freundlich, and Temkin isothermal adsorption equations are applied to describe the adsorption mechanism between the surface properties and adsorbent affinities of Cd (II)on biochars [22].

The Langmuir isotherm is expressed by Eq. 3:

$$\frac{c_e}{q_e} = \frac{1}{q_{max} b} + \frac{c_e}{q_{max}} \quad (3)$$

where C_e is the equilibrium concentration (mg/L), q_e is the equilibrium adsorption amount (mg/g), b (L/mg) is the Langmuir constant, and q_{max} is the maximum adsorption amount (mg/g).

The Freundlich isotherm is given as Eq. 4:

$$\log q_e = \log K_f + {}^{1}/_{n} \log C_e \quad (4)$$

In which, q_e is the equilibrium adsorption amount (mg/g), n and K_f (L/mg) are the Freundlich constants correspond to the biosorption capacity and surface heterogeneity, respectively, and C_e is the equilibrium concentration (mg/L).

The Temkin isotherm is expressed by Eq. 5:

$$q_e = \frac{RT}{b_T} \mathrm{Ln} K_T + \frac{RT}{b_T} \mathrm{Ln} C_e \quad (5)$$

In Eq. (5), b_T is the Temkin constant, K_T is the constant of equilibrium of Temkin (L/g), q_e (mg/g) and C_e (mg/L) are the adsorption capacity of biochars at the equilibrium and concentration of Cd (II) at the equilibrium, respectively. The ratio RT/b_T is assigned to the adsorption heat (J/mol), R is the perfect gas constant (8.314 J/mol K), and T is the temperature in kelvin.

2.4. Adsorption kinetics

Three kinetics models including pseudo-first-order, pseudo-second-order, and Elovich models were applied for determining the kinetics of Cd (II) adsorption on biochars. The factors of each model were determined by Eqs. (6), (7), and (8), respectively, [16]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \quad (7)$$

$$q_t = \frac{1}{\beta}\mathrm{Ln}(\alpha\beta) + \frac{1}{\beta}\mathrm{Ln}t \quad (8)$$

where k_1 (1/min) and k_2 (mg/g.min) are the rate constants of the pseudo-first-order equation and pseudo-second order equation, respectively. In Eq., 8 α (mg/g.min) is described as the initial Elovich adsorption rate and β (g/mg) is the Elovich desorption constant. q_e and q_t are the adsorption capacities (mg/g) at equilibrium and at time t (min), respectively.

3. Results and discussion

3.1. Characteristics of biochars

The FTIR spectra of the biochar and chitosan-modified biochar are shown in Figure 1. As shown in Figure 1, the specific functional groups of biochars contain 3410 cm^{-1} (–OH), 2923 cm^{-1} (–CH_2), 1799 cm^{-1} (C=O stretching), 1583 cm^{-1} (C=C and C=N, COO–), 1428 cm^{-1} (COOH and CHO, phenolic –OH bending, CO_3^{2-}), 1032 cm^{-1} (C–O stretching vibration in the ester group or phenol group), and 874 cm^{-1} (aromatic C–H) [21,33,45], 3415 cm^{-1} (–OH stretching), 2925 cm^{-1} (–CH_2), 1700 cm^{-1} (C=O stretching), 1577 cm^{-1} (the aromatic C=C and C=N stretching), 1420 cm^{-1} (C–O stretching vibration in the carboxylic acids group), 1000-1160 cm^{-1} (C-O stretching vibration in the ester group or phenol group) and 874 cm^{-1} (C–H bending) [8,13,37].

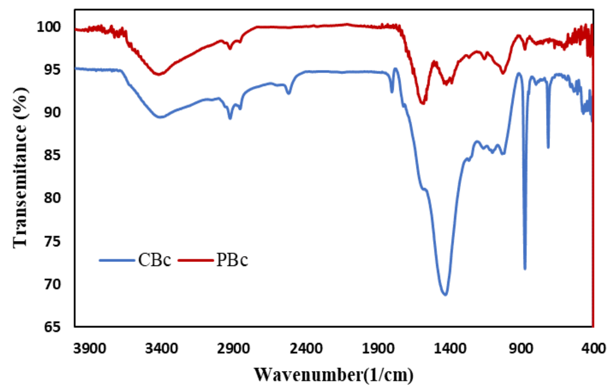

Fig.1. The FTIR spectra of pristine biochar and Chitosan-modified biochar

The microstructures were investigated by SEM imaging, Figure 3 a and b. According to Figure 3, compact and dense microstructure were observed in the pristine and chitosan modified biochar. Furthermore, some pores can be viewed. Table 1 shows the results of the BET surface area and pore volume of the samples and the CHN results. As specified in Table 1, the surface area of the biochar has increased with a modification of biochar using chitosan.

Table 1. BET surface area and pore volume of samples

Samples	BET			CHN		
	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	C (%)	H (%)	N (%)
PBc	3.108	0.012	16.317	72.12	2.12	0.82
CBc	3.748	0.009	10.429	65.30	4.11	3.38

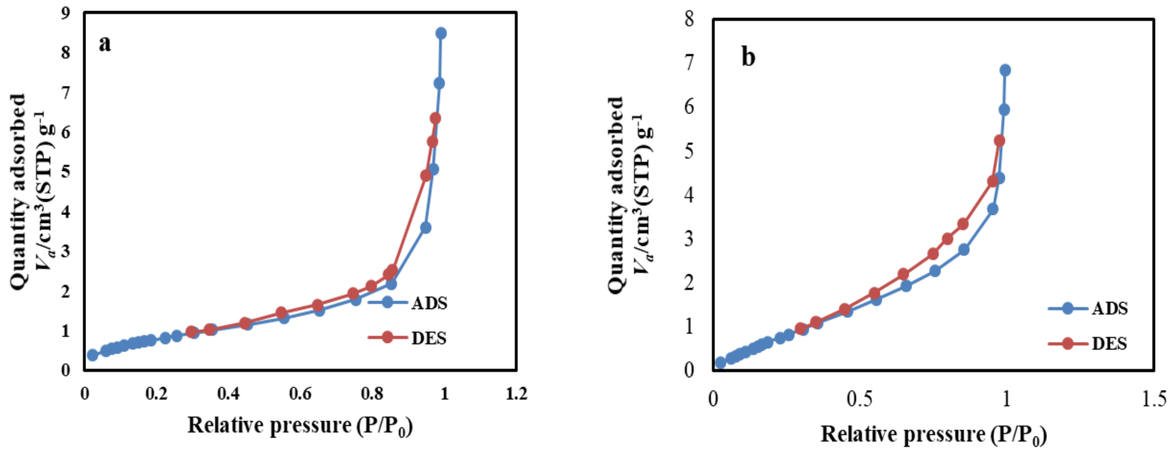

Fig. 2. (a) Nitrogen adsorption-desorption isotherms of PBc and (b) Nitrogen adsorption-desorption isotherms of CBc

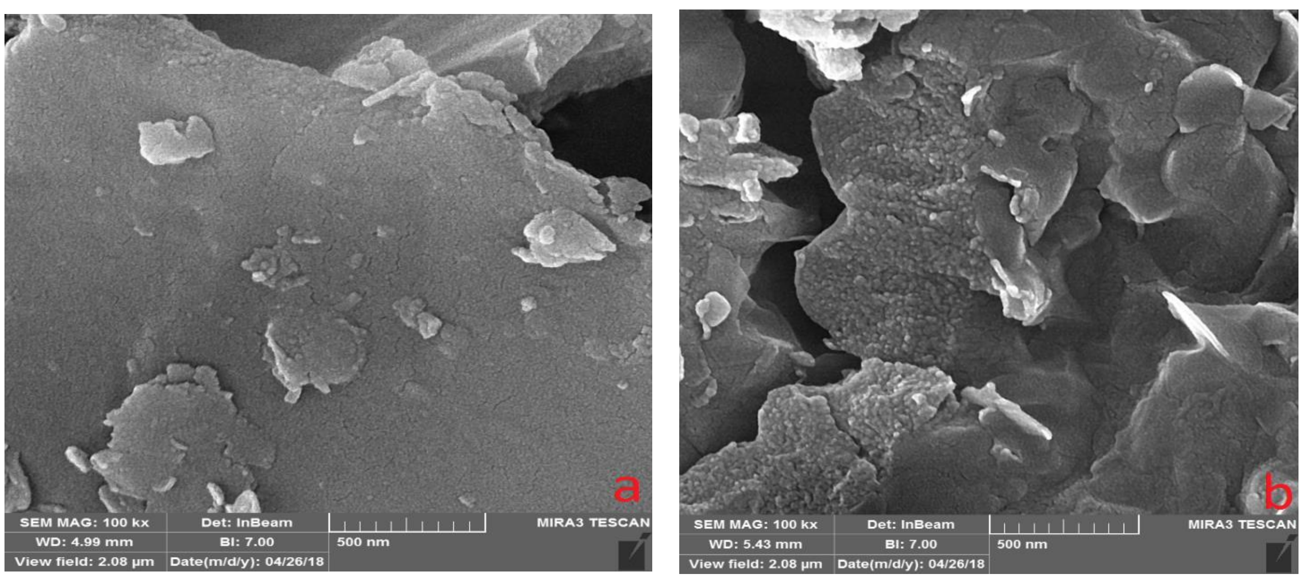

Fig. 3. SEM images of PBc (a) and CBc (b)

3.2. Effect of different parameters on Cd (II) adsorption

3.2.1. Effect of contact time

The effect of contact time (5-35 min) on the adsorption of Cd (II) by both biochars was assessed: constant biochar dosage (1 g/L), pH (7) and constant concentration (30 mg/L) of Cd (II). As seen in Figure 4, the percentage Cd (II) removal on the biochars increased with a rise in contact time up to 30 min, after that, the removal efficiency of Cd remained constant. The maximum removal of Cd (II) ions obtained at 30 min was 95% and 49% for CBc and PBc, respectively. The coating of the absorbents with chitosan and its combination with biochar can greatly improve the absorbent efficiency in the removal of heavy metals because its functional groups have the ability to form strong bonds with various metal ions [47]. Many research articles have proposed the chemical mechanism of the chitosan–metal ion binding process. Gerente, Lee, Cloirec and McKay [11] and Yang and Jiang [41] reported that metal adsorption by chitosan is probably absorbed through chelation and the formation of chitosan-metal complexes.

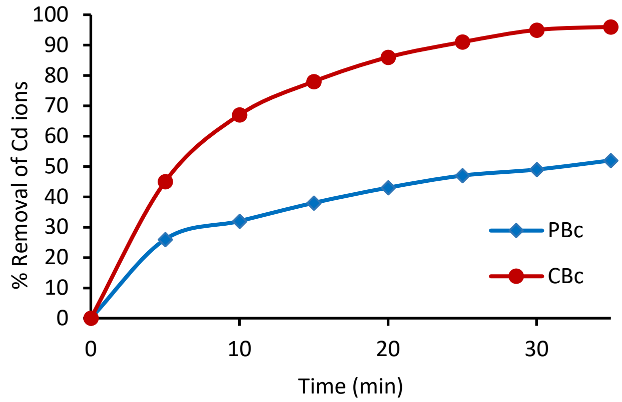

Fig. 4. Effect of contact time on the Cd (II) removal (at the reaction pH of 7 and the adsorbent dosage of 1 g/L)

3.2.2. Effect of adsorbent dosage

The effect of various amounts of biochars (ranging from 0.1 to 1 g/L) on Cd (II) removal was studied at 30 mg/L of initial Cd (II) concentration. According to Figure 5, with an increased amount of biochars beyond 0.6 g/L, the Cd (II) removal efficiency remained stable. the obtained optimized dosage of biochars is 0.6 g/L. Increasing adsorption is associated with the increase in the amount of adsorbent, and therefore, the capacity of ion exchange sites and also the active sites [2,29].

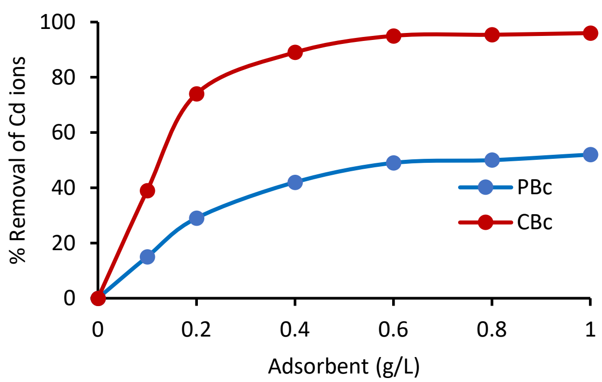

Fig. 5. Effect of adsorbent dosage on the Cd (II) removal (at the reaction pH of 7 and the optimum contacts time of 30 min**)**

3.2.3. Effect of pH

One more significant factor is pH, which also plays an important factor in Cd (II) adsorption on biochar. The percentage Cd (II) removal with the pH variation of (2-8) at a constant biochar dosage, time, and constant Cd (II) concentration is displayed in Figure 6. It is clear that the Cd (II) removal increased with increase in pH from 2 to 6, Fig 6. The results indicate a trend of reduced Cd (II) removal with increasing pH from 6 to 8. The low adsorption rate in acidic pH is due to the adsorption of H^+ on the biochar surface, which is competing with metal ions to adsorb on the biochar surface, as well as electrostatic repulsive between the adsorbent surface charge and the positive charge of metallic ions. This represents an ion exchange mechanism that may be included in the adsorption of metal oxide by metal ions. Similar results have been reported where biochar is derived from different materials [6,10,12,24]. Therefore, most researchers have reported that a pH level ranging from 5-6 is optimal for the adsorption of heavy metals [7,8]. Electrostatic interactions between Cd (II) and biochar is another possible adsorption mechanism at low pH [1].

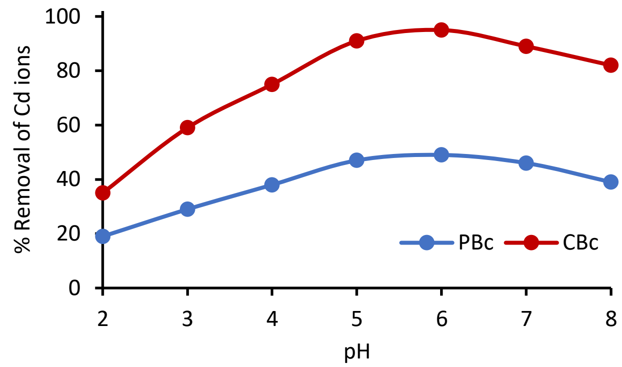

Fig. 6. Effect of pH on the Cd (II) removal (at the optimum adsorbent dosage of 0.6 g/L and the optimum contacts time of 30 min)

3.3. Isotherms models

The equilibrium isotherm of Cd (II) adsorption on biochars was described by the Langmuir, Freundlich, and Temkin models. The value of q_{max}, K, and R^2 in the Langmuir model was calculated from the linear plot between Ce/qe versus Ce. Also, the value of n, K_f, and R^2 in the Freundlich model and b_T, K_T, and R^2 in the Temkin model were determined from the linear plots of log q_e versus log C_e and qe versus ln Ce, respectively, Figure 7a, 7b, and 7c. These calculated correlation coefficients and adsorption parameters of the isotherm models are presented in Table 2. Based on the obtained results, the value of the correlation coefficient (R^2) for the Langmuir model (0.98 for PBc and 0.99 for CBc) was higher than the Freundlich model (0.92 for PBc and 0.72 for CBc) and the Temkin model (0.95 for PBc and 0.83 for CBc) for pristine and modified biochars, as shown in Table 2. Hence, the Langmuir isotherm model is the best fit to Cd (II) adsorption data. In the current study, the highest adsorption capacity (q_{max}) of chitosan-modified biochar determined from the Langmuir isotherm was 58.82 as compared to the pristine biochar.

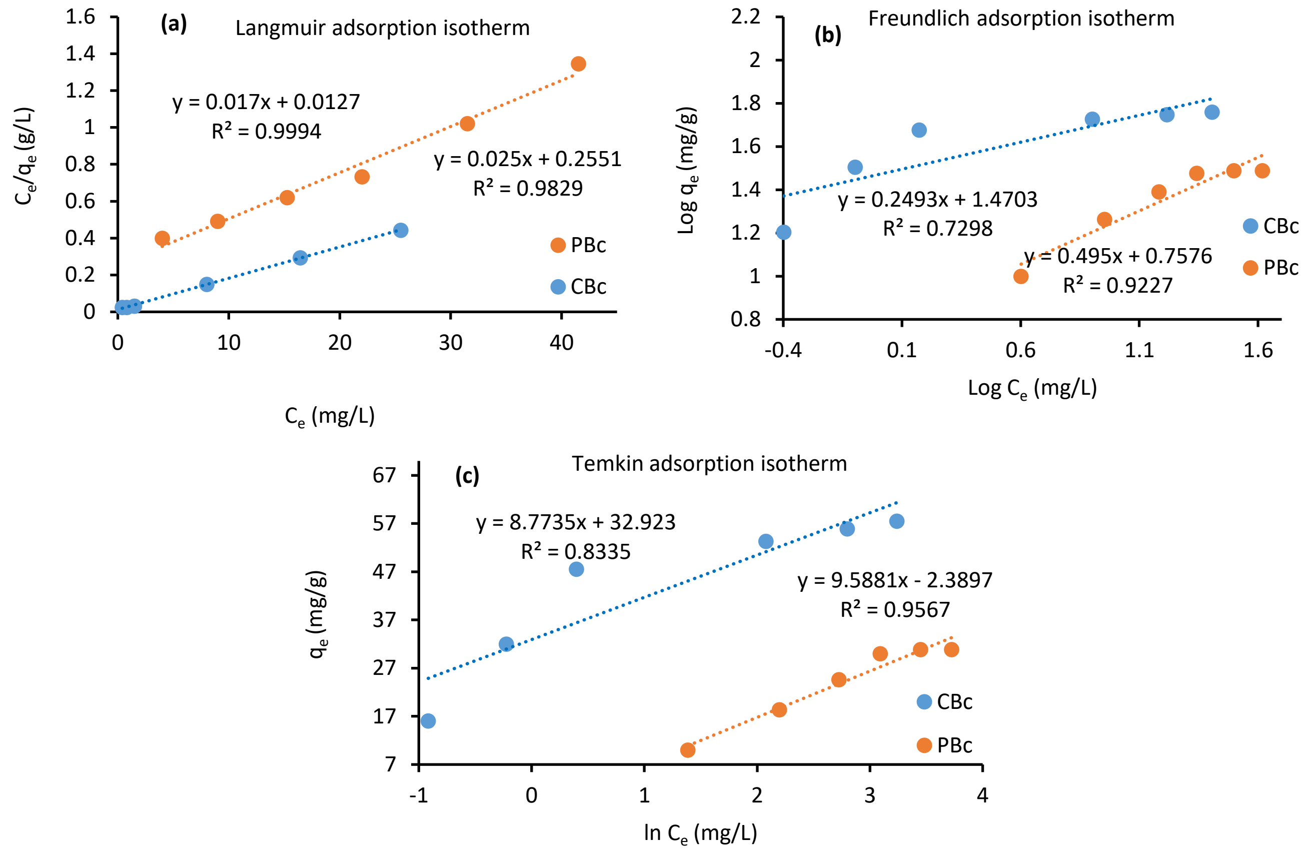

Fig. 7. Langmuir (a), Freundlich (b), and Temkin (c) isotherm plots for removal of Cd (II)

Table 2. Isotherm model for biochar and chitosan-modified biochar

Adsorbents	Langmuir Isotherm			Freundlich Isotherm			Temkin Isotherm		
	q_{max} (mg/g)	B (L/mg)	R^2	n	K_f (L/mg)	R^2	b_T (J/mol)	K_T (L/mg)	R^2
PBc	40	0.09	0.98	2.02	5.72	0.92	0.25	0.77	0.95
CBc	58.82	1.33	0.99	4.01	29.53	0.72	0.28	42.62	0.83

3.4. Kinetic models

The results of the kinetic data display the Cd (II) adsorption rate on the surface on biochars expressed by pseudo-first-order, pseudo-second-order, and Elovich models. A comparison of the three fitted kinetic data of the biochars shown in Figure 8a, 8b and 8c indicate that the correlation coefficient (R^2) for the pseudo-second-order model (0.99 for PBc and 0.99 for CBc) was greater than the pseudo-first-order (0.98 for PBc and 0.91 for CBc) and Elovich model (0.98 for PBc and 0.98 for CBc). Thus, it can be concluded that the kinetic model of Cd (II) adsorption by both biochars is described by the second-order kinetic model. The results of the kinetic model parameters are listed in Table 3.

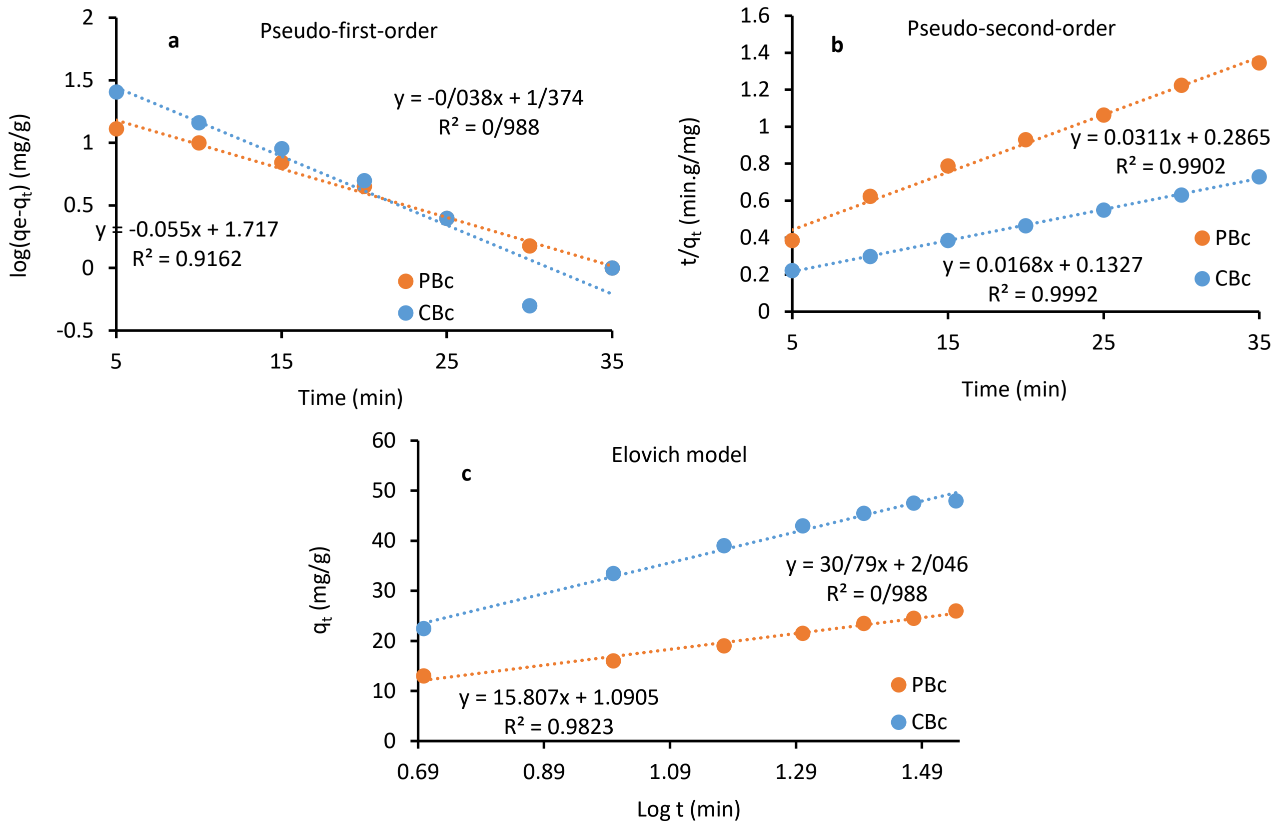

Fig. 8. Linear plots of pseudo-first order (a), pseudo-second order (b), and Elovich (c) kinetic models for removal of Cd (II)

Table 3. Kinetics fitting parameters of Cd (II) adsorption on biochars

Biochars	Pseudo-first-order			Pseudo-second-order			Elovich		
	q_e	K_1	R^2	q_e	K_2	R^2	α	β	R^2
PBc	23.69	0.08	0.98	32.15	0.003	0.99	16.93	0.06	0.98
CBc	52.11	0.12	0.91	59.52	0.002	0.99	32.90	0.03	0.98

The maximum biosorption capacities of biochars with other adsorbents, including biochar for the Cd (II) removal, are listed in Table 4. The results show that the chitosan-modified biochar is superior to some of the other adsorbents in terms of its availability, the cost-effectiveness of peanut shell biochar, and the maximum biosorption capacity of cadmium ions.

Table 4. List of the biochars with various adsorbents

Adsorbents	q_{max} (mg/g)	Reference
Magnetic oak wood biochar	3	[23]
Blast furnace slag	3.78	[26]
Fly ash	5.05	[26]
Polyelectrolyte-coated fly ash	6.3939	[27]
Magnetic oak bark biochar	7.3	[23]
Giant Miscanthus biochar	12.96	[18]
Unmodified nano-clay	19.52	[25]
Magnetic ChNTs	23.8	[44]
$KMnO_4$ modified Biochar	28.104	[38]
Fe_3O_4 nanoparticles loaded	51	[17]
Magnetic biochar	62.50	[30]
PBc	40	This study
CBc	58.823	This study

4. Conclusions

In this work, the maximum Cd (II) adsorption capacity between PBc and CBc was investigated. The results showed that the biosorption of Cd (II) on the biochars was dependent on the biochar dosage, pH, and contact time. Optimum conditions for the highest removal of Cd (II) were obtained at a biochar dosage of 0.6 g/L, a 30 mg/L initial concentration of Cd (II) solution, a pH value of 6, and within 30 minutes. CBc is more competent in Cd (II) removal compared with PBc, 95% and 49%, respectively. The Langmuir maximum adsorption capacity of PBc and CBc were determined to be 40 and 58.82 mg/g, respectively. The pseudo-second-order model best fitted the experimental data.

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